Oxidation of CH_3NH_2 and $(CH_3)_2NH$ by $Ni^{III}(cyclam)(H_2O)_2{}^{3+}$ in Aqueous Solutions

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Ni^{II}(1,4,8,11-tetraazacyclotetradecane)$^{2+}$, $Ni^{II}L^{2+}$, is a good electrocatalyst for the oxidation of CH_3NH_2 and $(CH_3)_2NH$ but not of $(CH_3)_3N$. The oxidation kinetics of the amines by $Ni^{III}L(H_2O)_2{}^{3+}$ indicate that the amines are good axial ligands to the tervalent nickel complex. The complexes $Ni^{III}L[N(CH_3)_iH_{3-i}](H_2O)^{3+}$ are stronger oxidants than the complexes $Ni^{III}L[N(CH_3)_iH_{3-i}]_2{}^{3+}$. The oxidation is base-catalyzed and obeys a second-order rate law in $Ni^{III}LX_2$. It is proposed that the key step is $Ni^{III}–L(H_2O)[N(CH_3)_iH_{2-i}]^{2+} + Ni^{III}LX_2 \rightarrow LNi^{II}–N(=CH_2)(CH_3)_{i-1}H_{2-i} + Ni^{II}L^{2+} + H_3O^+ + 2\ X$. Naturally, $N(CH_3)_3$ is not oxidized by this mechanism. Of special interest is the observation that the axial ligands CH_3NH_2 and $(CH_3)_2NH$ are oxidized by the central cation, while the cyclam ligand, which has four secondary amine groups bound to the nickel(III) ion, and axially bound pendant primary amine groups, which are covalently linked to the macrocyclic ligand, are relatively stable. This difference in the behavior of axially bound amine groups is attributed to the free rotation of the axially bound $N(CH_3)_iH_{3-i}$ ligands that is required for the oxidation to proceed.

Introduction

$Ni^{III}L^i(H_2O)_2{}^{3+}$ complexes, where L^i is a neutral tetraazamacrocyclic ligand, are stabilized by axial coordination of a variety of anions.[1–3] The $Ni^{III}L^i$ complexes are also stabilized by pendant amine substituents of the macrocyclic ligands, which are capable of binding axially to the central nickel cation.[4–7] Therefore, it seemed reasonable to try and stabilize $Ni^{III}L^i(H_2O)_2{}^{3+}$ complexes by axial coordination of amines. As the ligating groups of L^i are four secondary amines and as the pendant substitutes studied were primary amines,[4–7] it seemed reasonable to assume that axially bound amines will not be oxidized by the central Ni^{III} cation. Surprisingly, it was observed that $Ni^{II}L^{2+}$, where L = 1,4,8,11-teraazacyclotetradecane, is an electrocatalyst for the oxidation of CH_3NH_2 and $(CH_3)_2NH$. The mechanism of the oxidation of the amines was studied and the plausible reasons for the different oxidation resistance of free axial and pendant amines are discussed.

Results and Discussion

Electrochemistry

Cyclic voltammograms of NiL^{2+} in the presence of methylamine and dimethylamine (Figures 1 and 2) clearly demonstrate that the nickel complex is an electrocatalyst for the oxidation of these amines. On the other hand, the voltammogram in the presence of trimethylamine (Figure 3) reveals that this amine is not electrocatalytically oxidized in the presence this complex. From the small shift of the wave in the presence of $N(CH_3)_3$, the pH, and the pK_a of $HN(CH_3)_3{}^+$ (pK_a = 9.8) one can calculate, with the use of the Nernst equation, that the binding constant of $N(CH_3)_3$ to $Ni^{III}L(H_2O)_2{}^{2+}$ is smaller than $4.0 \times 10^5\ \text{M}^{-1}$.

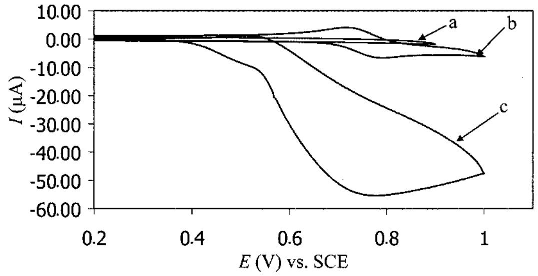

Figure 1. Voltammogram of NiL^{2+} in the presence of methylamine; solution composition: pH = 7.0; 0.1 M ($NaClO_4$); a: $NH_3CH_3{}^+$ 0.02 M; b: NiL^{2+} 0.0001 M; c: $NH_3CH_3{}^+$ 0.02 M, NiL^{2+} 0.0001 M; scan rate 50 mV/s

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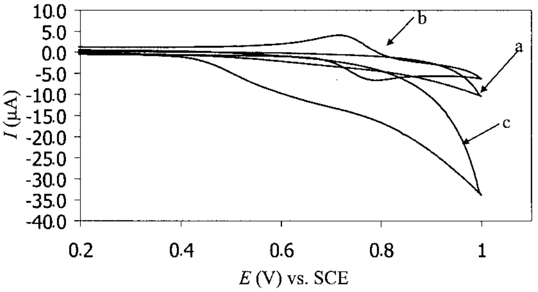


Figure 2. Voltammogram of NiL^{2+} in the presence of dimethylamine; solution composition: pH = 7.0; 0.1 M ($NaClO_4$); a: $NH_2(CH_3)_2^+$ 0.02 M; b: NiL^{2+} 0.0001 M; c: $NH_2(CH_3)_2^+$ 0.02 M, NiL^{2+} 0.0001 M; scan rate 50 mV/s

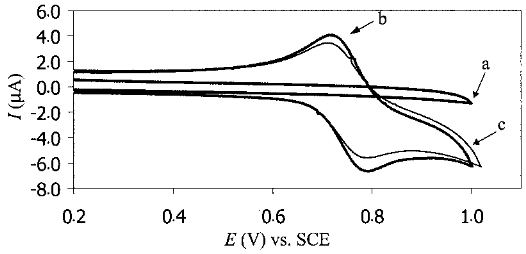


Figure 3. Voltammogram of NiL^{2+} in the presence of trimethylamine; solution composition: pH = 7.0; 0.1 M ($NaClO_4$); a: $NH(CH_3)_3^+$ 0.02 M; b: NiL^{2+} 0.0001 M; c: $NH(CH_3)_3^+$ 0.02 M, NiL^{2+} 0.0001 M; scan rate 50 mV/s

Kinetic Studies

When solutions containing 0.0001 M $Ni^{III}L(SO_4)_2^-$ are mixed with excess $NH_3CH_3^+$ or $NH_2(CH_3)_2^+$ at a constant ionic strength of 0.1 M ($NaClO_4$), fast disappearance of the spectrum due to the complex $Ni^{III}LX_2$ is observed, see for example Figure 4. The kinetics of this process fit a second-order rate law with respect to $[Ni^{III}LX_2]$.

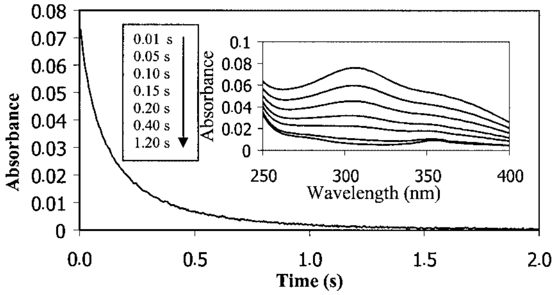


Figure 4. Oxidation of $NH_3CH_3^+$ by $Ni^{III}L(SO_4)_2^-$ at pH = 7.0; solution composition: $NH_3CH^+{}_3$ 0.01 M; $Ni^{III}L(SO_4)_2^-$ 0.0001 M; BIS TRIS buffer 0.0001 M; measured at 306 nm; inset: time-dependent spectra of the solution

Table 1. Observed rates for the oxidation of amines by $Ni^{III}L(SO_4)_2^-$; solution composition: $NiL(SO_4)_2^-$ 0.0001 M; BIS TRIS buffer 0.0001 M; pH = 7.0

$2k$ [$M^{-1}s^{-1}$] for $NH_2(CH_3)_2^+$	$2k$ [$M^{-1}s^{-1}$] for $NH_3CH_3^+$	$NH_3CH_3^+$/ $NH_2(CH_3)_2^+$ [M]
5550 ± 50	49.0 ± 0.3	1.60×10^{-2}
5750 ± 50	63.5 ± 0.3	1.25×10^{-2}
5850 ± 40	72.5 ± 0.4	1.00×10^{-2}
5950 ± 40	85.0 ± 0.4	5.00×10^{-3}
6250 ± 50	88.0 ± 0.5	2.50×10^{-3}
6350 ± 50	92.0 ± 0.8	1.60×10^{-3}
6400 ± 50	97.0 ± 0.8	1.25×10^{-3}

Surprisingly, when the concentration of the amines is changed at constant pH, the rates of the processes decrease somewhat with an increase in the concentration of the amines (Table 1). These results clearly indicate that the equilibria according to Equations (1)−(3) exist in solution and that $Ni^{III}L[N(CH_3)_iH_{3-i}]_2^{3+}$ is more stable than $Ni^{III}L(H_2O)[N(CH_3)_iH_{3-i}]^{3+}$.

$$Ni^{III}L_{aq} + N(CH_3)_iH_{3-i} \rightleftarrows Ni^{III}L(H_2O)N(CH_3)_iH_{3-i}{}^{3+} \; (i = 1 \text{or } 2) \tag{1}$$

$$Ni^{III}L(H_2O)N(CH_3)_iH_{3-i}{}^{3+} + N(CH_3)_iH_{3-i} \rightleftarrows Ni^{III}L[N(CH_3)_iH_{3-i}]_2{}^{3+} + H_2O \tag{2}$$

$$N(CH_3)_iH_{3-i} + H_3O^+ \rightleftarrows N(CH_3)_iH_{4-i}{}^+ \tag{3}$$

The maximum rate is observed at the lowest amine concentration studied, $[N(CH_3)_iH_{4-i}]^+ = 1.25 \times 10^{-3}$ M at pH = 7.0. This result indicates that already at this concentration at least one amine is bound to the nickel complex. From this value, assuming that at least 90% of the nickel(III) complexes have at least one bound amine at this pH, one calculates:

$$K_{1app} = \frac{[Ni^{III}L(H_2O)\{N(CH_3)_iH_{3-i}\}^{3+}]}{[Ni^{III}L(H_2O)_2{}^{3+}]\,[N(CH_3)_iH_{4-i}{}^+]} \geq 10 / 1.25\times10^{-3} = 8\times10^{3}\,M^{-1}$$

As the pK_a values of $N(CH_3)H_3^+$ and $N(CH_3)_2H_2^+$ are 10.64 and 10.72, respectively, one calculates from the results that (Supporting Information; see footnote on the first page of this article):

$$K_1 = \frac{[Ni^{III}L(H_2O)N(CH_3)H_2{}^{3+}]}{[Ni^{III}L(H_2O)_2{}^{3+}][N(CH_3)H_2]} \geq 3.4\times10^{7}\,M^{-1}$$

$$K_1 = \frac{[Ni^{III}L(H_2O)N(CH_3)H_2{}^{3+}]}{[Ni^{III}L(H_2O)_2{}^{3+}][N(CH_3)_2H]} \geq 4.1\times10^{7}\,M^{-1}$$

The estimation of the stability constant for the binding of the second amine molecule is considerably more difficult:

$$K_2 = \frac{[Ni^{III}L\{N(CH_3)_iH_{3-i}\}_2{}^{3+}]}{[Ni^{III}L(H_2O)\{N(CH_3)_iH_{3-i}\}^{3+}][N(CH_3)_iH_{3-i}]}$$

For this calculation one has to make one of two assumptions:

a) The rate of decomposition of $Ni^{III}L[N(CH_3)_iH_{3-i}]_2^{3+}$ is negligible relative to that of $Ni^{III}L(H_2O)[N(CH_3)_iH_{3-i}]^{3+}$. With this assumption, a lower limit for K_2 can be calculated.

b) The observed rate of decomposition at the highest concentration of $N(CH_3)_iH_{4-i}^{+}$ used is the rate of decomposition of $Ni^{III}L[N(CH_3)_iH_{3-i}]_2^{3+}$. With this assumption, an upper limit for K_2 is calculated.

Thus, $4.8 \times 10^5 < K_2 < 9.6 \times 10^6$ M^{-1} and $4.0 \times 10^5 < K_2 < 8.9 \times 10^6$ M^{-1} for $N(CH_3)H_2$ and $N(CH_3)_2H$, respectively, are obtained.

The pH effect on the rates of oxidation of CH_3NH_2 and $(CH_3)_2NH$ by $Ni^{III}L(SO_4)_2^-$ was studied. The results (Figure 5) indicate that the rate depends linearly on $[OH^-]$ over the entire pH range studied. This result is in agreement with the expectation that the axially bound amine has a pK_a, i.e. that one of its protons is lost and that the alkaline form $N(CH_3)_iH_{2-i}^{2+}$ is the one that is oxidized:

$$LNi^{III}-N(CH_3)_iH_{3-i}^{3+} + OH^- \rightleftarrows LNi^{III}-N(CH_3)_iH_{2-i}^{2+} + H_2O$$

The results indicate that the pK_a s of the bound amines are ≥ 10. The latter finding is in agreement with the suggestion that the secondary amines of the macrocyclic ligands in the Ni^{III} complexes have pK_a values > 10.[8]

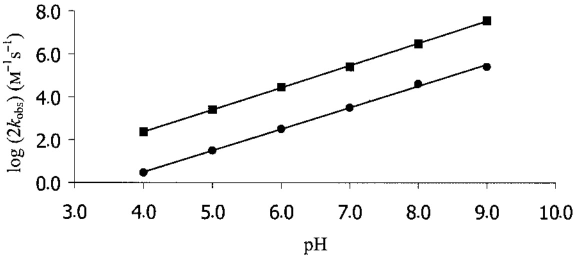
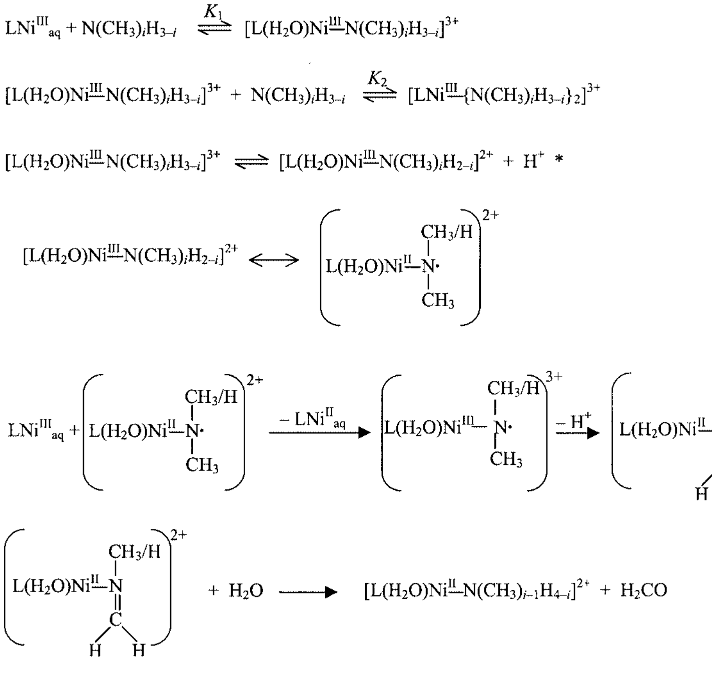


Figure 5. Dependence of the observed rate of oxidation of $NH_3CH_3^+$ (circles) and $NH_2(CH_3)_2^+$ (squares) on pH; solution composition: $NH_3CH_3^+/NH_2(CH_3)_2^+$ 0.01 M; $Ni^{III}L(SO_4)_2^-$ 0.0001 M; BIS TRIS buffer 0.0001 M (pH range 5.8−7.2); TRIS BASE buffer 0.0001 M (pH range 8.0−9.0); TRIS ACID buffer 0.0001 M (pH range 4.0−5.0)

Thus, the kinetic results agree with the following mechanism for the oxidation of CH_3NH_2 and $(CH_3)_2NH$ by $Ni^{III}L(H_2O)_2^{3+}$; As the concentration of SO_4^{2-} in solution is 2×10^{-4} M, the complex loses the sulfate ligands when dissolved:[9]



* For simplicity only this possibility is drawn; however, clearly analogous reactions for $[LNi^{III}(N(CH_3)_iH_{3-i})_2]^{3+} \rightleftharpoons [L\{N(CH_3)_iH_{3-i}\}Ni^{III}N(CH_3)_iH_{2-i}]^{2+} + H^+$ have to be considered.

This mechanism is in agreement with the suggested mechanism for the oxidation of the macrocyclic ligand by the central Ni^{III} ion, which occurs considerably slower.[8]

As the $N(CH_3)_iH_{3-i}$ ligands stabilize the central Ni^{III} ion by lowering the oxidation potential of the complex, $LNi^{III}-[N(CH_3)_iH_{3-i2}]$ decomposes slower than $L(H_2O)Ni^{III}N(CH_3)_iH_{3-i}$.

The proposed mechanism predicts that H_2CO will be one of the products of the reaction. Indeed, analysis indicates that the yield of H_2CO is 42 ± 4% of the $Ni^{III}L(SO_4)_2^-$

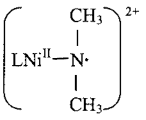
used; this is in good agreement with the proposed mechanism.

Concluding Remarks

The results point out two relatively unexpected conclusions:

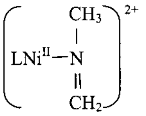
1. The binding constant of $N(CH_3)_3$ to $Ni^{III}L(H_2O)_2{}^{3+}$ is smaller by over two orders of magnitude than that of CH_3NH_2 and $(CH_3)_2NH$. This result is in agreement with previous results that show that tertiary amines are poor ligands to high-valent transition metal cations due to their hydrophobic nature.[10–12]

2. The free axial ligands $(CH_3)NH_2$ and $(CH_3)_2NH$ are oxidized faster by many orders of magnitude than axial pendant primary amines, which are bound as substituents to the macrocyclic ligand. The source of this difference seems to be that the transformation of



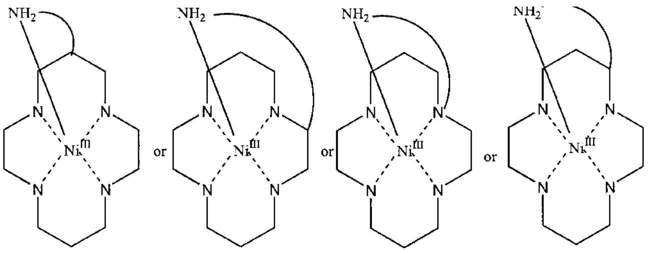
$$\left(\begin{array}{c} \quad CH_3 \\ \quad | \\ LNi^{II}{-}N\cdot \\ \quad | \\ \quad CH_3 \end{array}\right)^{2+}$$

into



$$\left(\begin{array}{c} \quad CH_3 \\ \quad | \\ LNi^{II}{-}N \\ \quad \| \\ \quad CH_2 \end{array}\right)^{2+}$$

through oxidation requires a relatively free rotation around the $N-CH_3$ bond. This rotation is hindered around the C−N bonds of the macrocyclic ligand and around the C−N bonds in complexes with the general structure:



A similar interpretation was given previously to explain the different stabilities of the *rac* and *meso* diastereoisomers of Ni^{III}(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)$^{3+}$.[8]

Experimental Section

Materials: The ligand L = 1,4,8,11-tetraazacyclotetradecane and the complex $Ni^{II}L(ClO_4)_2$ were synthesized by a previously reported method.[13] All other chemicals used were of analytical grade, and were used without further purification. All solutions were prepared with heat-distilled water, which was further purified by passing through a Millipore Milli-Q water purification system, to a final resistance $>10\ {}^{m}\Omega$.

Preparation of $Ni^{III}L(SO_4)_2$: The tervalent complex was prepared by oxidation of $Ni^{II}L^{2+}$ by $Na_2S_2O_8$ at pH = 3.0. The complex thus prepared is relatively stable in aqueous solutions, $t_{1/2}$ = several hours.[9] The yield was determined spectrophotometrically by measuring the absorption at $\lambda = 306$ nm ($\varepsilon = 9600\ \text{M}^{-1}\text{cm}^{-1}$).[9]

Electrochemical Procedures: Cyclic voltammetric studies were carried out using an EG&G Princeton Applied Research potentiostat/galvanostat, model 263 A, operated by a Research Electrochemistry software EG&G PARC, with a three-electrode assembly consisting of a glassy carbon working electrode ($A = 0.07\ \text{cm}^2$), a platinum counter electrode, and a saturated calomel electrode as the reference electrode.

Kinetic Studies: Slow reactions were monitored spectrophotometrically with an HP 8452-A diode array spectrophotometer, in an anaerobic UV/Vis quartz cell. Fast reactions were studied with a stopped-flow Applied Photo Physics, Model SX 18-MV apparatus.

H_2CO Analysis: Formaldehyde was determined by a colorimetric method[14] from its yellow complex with acetyl acetone (diacetyldihydrolutidine) measuring the absorption at 412 nm.

Acknowledgments

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